

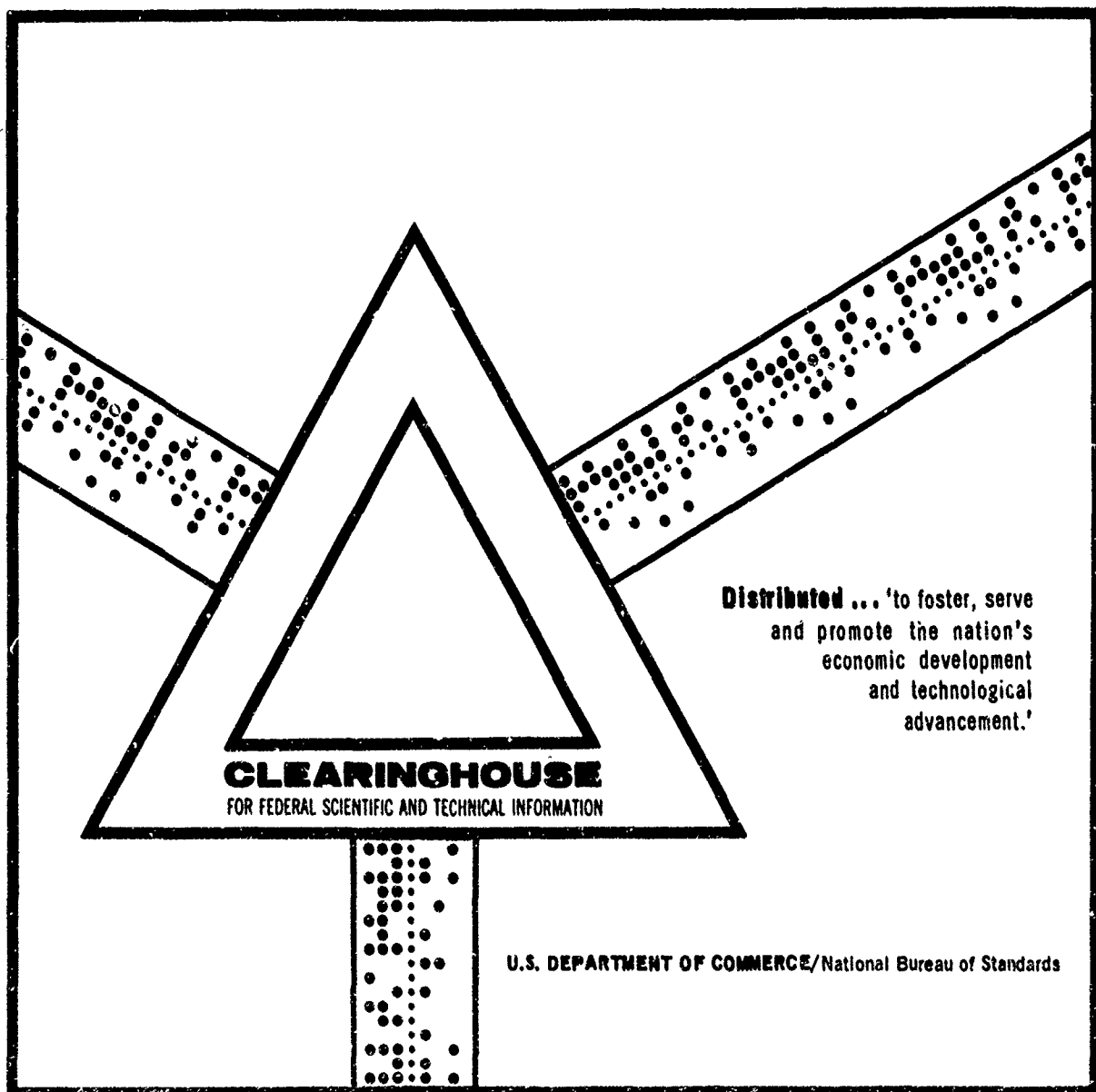
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THERMODYNAMIC PROPERTIES OF TERNARY REFRACTORY CARBIDES. IV. RELATIONS BETWEEN THERMODYNAMIC PROPERTIES, BONDING, AND COMPRESSIBILITY

M. Hoch, et al

Cincinnati University  
Cincinnati, Ohio

December 1969



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AFML-TR-89-209  
PART IV

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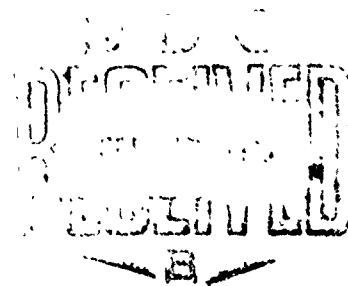
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*M. HOCH and S. YAMAUCHI*

TECHNICAL REPORT AFML-TR-89-209, PART IV

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## FOREWORD

This report was prepared by the University of Cincinnati under Contract No. F33615-67-C-1565. This work was initiated under Project No. 7360, "Chemical, Thermal, and Dynamic Properties of Materials," Task 736005, "Compositional, Atomic, and Molecular Analysis." This research was supported in part by the National Aeronautics and Space Administration Research Grant NGR 36-004-014. The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command with Mr. Freeman F. Bentley as Project Engineer.

This report covers work conducted from July 1, 1967 through June 30, 1969. Manuscript was released in July by the authors for publication as an Air Force Materials Laboratory Technical Report.

The work was performed at the Materials Science Laboratory at Wright-Patterson Air Force Base, with Dr. Michael Hock serving as the Principal Investigator.

This report has been reviewed and is approved.

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Chief, Analytical Branch  
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## ABSTRACT

The high temperature thermodynamic data obtained on ternary carbides having the sodium-chloride type structure have been correlated with the bonding and mechanical properties of these carbides. The metal-metal bonding on the metal sublattice in the carbide is the same as in the binary body-centered cubic metals. The variation of the carbon-carbon interaction energy and the metal-carbon interaction energy indicates that the metal-carbon bonds are localized bonds. From the variation of the difference in metal-carbon interaction energy with composition the compressibility of the carbides at elevated temperature can be calculated. The values are in excellent agreement with values derived from room temperature mechanical properties measurements.

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## INTRODUCTION

In a previous paper,<sup>1</sup> Hoch has investigated the binary pairwise interaction energies in compounds having the sodium-chloride type structure. As pointed out in that paper, the energies show a certain regularity. The values for zirconium, hafnium, and niobium carbide are reproduced here in Table I together with the values of uranium carbide derived later.<sup>2</sup> The nomenclature is changed somewhat so that 1 refers to zirconium, 2 to hafnium, niobium, or uranium, and 3 to carbon.

In subsequent papers, Jun and Hoch,<sup>3</sup> Hapase and Hoch,<sup>4</sup> and Yamauchi and Hoch<sup>5</sup> have studied the activities of the components in the single phase NaCl type structure in zirconium-niobium-carbon,<sup>3</sup> zirconium-uranium-carbon,<sup>4</sup> and zirconium-hafnium-carbon,<sup>5</sup> and from these data derived the pairwise interaction energies or their differences between the various atoms. The present paper will attempt an interpretation of the thermodynamic results based on pairwise bonding between atoms and will calculate the compressibility from the thermodynamic measurements.

The paper of Jun and Hoch<sup>3</sup> indicated that the carbon-carbon interaction energy in the ternary zirconium-niobium-carbide varied parabolically with composition:

$$E_{33} = 15.62 + 9.37x - 29.50(1-x)x \text{ kcal/mole.}$$



This already has indicated that the bonding is very localized in the system because to obtain this type of variation with composition, one must have carbon atoms attached to niobium, and carbon atoms attached to zirconium.<sup>3</sup>

The model used for the statistical thermodynamic derivation has been discussed earlier;<sup>12,13</sup> it will only be summarized here. The standard state for all the element is the pure, condensed element at the temperature in question. The atoms are distributed randomly over the available sites; this is equivalent to the regular solution. However, the error due to this in obtaining the interaction parameters is very small. By assuming first ordered, then randomly distributed atoms, the pairwise interaction energy changed only 10% in the case of NbO.<sup>12</sup> The grand partition function was set up with pairwise interaction energies  $E_{ij}$  which are independent of composition.<sup>13</sup> It is possible to introduce correction terms into the grand partition function of the form  $E_{ijk}$  (this is the energy term correcting the  $E_{ij}$  energy when an atom  $k$  is present next to the  $ij$  bond), or of the form  $E_{ijki}$  (correction terms to the  $E_{ij}$  energy when a bond  $ki$  is next to the  $ij$  bond). This way the  $E_{ij}$  can be made composition dependent. This has been done in the case of tantalum-hydrogen system.<sup>12</sup>

The model neglects the small amount of Schottky defects present and therefore it is only valid when  $1-y \gg \delta$ ,  $\delta$  being concentration of Schottky defects.

## EXPERIMENTAL RESULTS AND DISCUSSION

The metal-metal interaction energy on the metallic sublattice was determined in three cases and also was calculated from the binary metal phase diagrams. The data are given in Table II. In Table II, the metal to metal distances in pure elements as calculated from Darken and Gurry<sup>6</sup> and those in the carbides as determined in the previous investigations are given. Table II shows that the metal-metal distance in the carbides is about 10% larger than the metal-metal distance in the pure b.c.c. metals. Also, the metal-metal interaction energy on the metal sublattice in the carbide is 2 kcal/mole larger than that in the b.c.c. metal phase.

This difference of 2 kcal/mole can be attributed to the transformation of the b.c.c. structure to a f.c.c. structure and mostly to the expansion of the metal-metal distance. Thus, one can conclude that the metal to metal bonding in the carbides is the same as in the pure metallic systems.

One of the results of the previous investigations<sup>3,4,5</sup> was that the value of  $[E_{13}-E_{23}]$ , the bonding difference between zirconium-carbon bond and the other metal-carbon bond, is not constant, but varies linearly with composition. The equations obtained for  $[E_{13}-E_{23}]$  are given in Table III. The variation of the metal-carbon interaction energy difference with composition again suggests that one has to deal with localized metal to carbon bonds which as the composition changes get compressed or expanded.

To explain the behavior of the carbides, one will have to look at an energy potential-distance diagram of a metal-carbon bond, as is shown in Figure 1. If the lattice parameter of the various carbides, and thus the amount of compression or expansion of each metal-carbon bond is not too great, one can restrict himself to the bottom of the potential well, and he can express the two interaction energies parabolically as follows:

$$E_{13} = \alpha_1 (r-r_1)^2 + E_{13}^{\circ} \quad (1)$$

$$E_{23} = \alpha_2 (r-r_2)^2 + E_{23}^{\circ} \quad (2)$$

where  $E_{13}^{\circ}$  and  $E_{23}^{\circ}$  are the metal-carbon interaction energies in the binary carbides,  $r_1$  and  $r_2$  are the metal-carbon distances in the binary carbides, and  $r$  is the average metal-carbon distance in a ternary carbide (obtained from lattice parameters), and  $E_{13}$  and  $E_{23}$  are the metal-carbon interaction energies in the ternary carbide.  $\alpha_1$  and  $\alpha_2$  are the compressibilities of the two carbides.  $[E_{13}-E_{23}]$  would be the difference between the equations (1) and (2). As the compressibilities of the carbides are not too different at room temperature (see Table III), it can also be assumed that they are not too much different at 2500°K, and thus, in first approximation,  $\alpha_1 \approx \alpha_2 \approx \alpha$ . So we finally obtain:

$$E_{13}-E_{23} = \alpha (r_2-r_1) [2r-(r_1+r_2)] + E_{13}^{\circ}-E_{23}^{\circ}. \quad (3)$$

The lattice parameters in the ternary carbides at constant carbon content vary linearly with metal composition<sup>3,4,5</sup>

$$r = r_2 + x(r_1 - r_2). \quad (4)$$

Combining equations (3) and (4),

$$E_{13} - E_{23} = E_{13}^{\circ} - E_{23}^{\circ} - 2\alpha(r_1 - r_2)^2(x - 0.5). \quad (5)$$

This equation indicates that  $[E_{13} - E_{23}]$  should be equal to  $[E_{13}^{\circ} - E_{23}^{\circ}]$  when  $x = 0.5$ . These values are calculated in Table IV from the thermodynamic data on ternary carbides in Table III, and also calculated from binary data in Table I. In using the data in Table I, it is assumed that  $E_3 + E_{33}$  is the same in all of the carbides investigated.  $E_3 + E_{33}$  is the energy required to take a carbon atom from its standard state (graphite), put it on the carbon sublattice, and then have the carbon atoms interact pairwise with each other. The agreement between the two values is good.

The value of  $\alpha$ , which is related to the compressibility of the carbide, can now be calculated from the variation of  $[E_{13} - E_{23}]$  with composition.

$\alpha$  can also be calculated, using the method of Slater,<sup>7</sup> to treat the cohesive energy of the metals. According to Slater,<sup>7</sup>

$$\alpha = N_0 c r_0 (9/2) P \quad (6)$$

where  $N_0$  is Avogadro's number;  $c$  is a constant, such that the volume per molecule is  $c r_0^3$  and  $c = 2$  in the NaCl type structure;  $r_0$  is the nearest-neighbor distance; and  $P$  is the bulk modulus or  $P = 1/\beta$  where  $\beta$  is the compressibility. The results of the calculations are shown in Table V by using equation (5) and the values in Table III.

Looking at Table V-B, one sees that  $\alpha$  is almost the same for all the carbides used in the present investigation; thus, the assumption  $\alpha_1 = \alpha_2 = \alpha$  used earlier seems to be justified. It must be kept in mind that the values of  $\alpha$  derived in Table V-B are obtained from data at room temperature and were carried out on polycrystalline materials. The values obtained in Table V-A from the thermodynamic data are at 2500°K and represent values for single crystals.

The value of  $\alpha$  in the zirconium-hafnium-carbon system is very high. This is due to the very small difference in interatomic radii, where a small error can effect the value of  $\alpha$  greatly.

The values obtained from thermodynamic measurements and from room temperature compressibility are of the same order of magnitude. The average value of  $\alpha$  for zirconium and niobium carbide is 8 and compares with the value of 5.6 obtained from high temperature thermodynamic measurements. Similarly, the average value for zirconium-carbon and uranium-

carbon is 5.9, comparing with 4.8 obtained from high temperature thermodynamic measurements. The value in the Zr-Hf-C system of 43.5 for  $\alpha$  can be disregarded because in calculating  $E_{12}-E_{13}$   $\alpha (r_1 - r_2)^2$  is very small, giving a very uncertain value. It is possible to draw a line through the experimental points and determine  $E_{12}-E_{13}$  in such a fashion that the composition dependent term becomes zero.

The compressibility increases with increasing temperature, and thus,  $\alpha$  should decrease. This is found in the values in Table V where the thermodynamic values (at 2500°K) are lower than the room temperature compressibility values.

The only comparison available is that with the results of Speck,<sup>8</sup> who measured elastic constants of polycrystalline  $\text{NbC}_{0.97}$  having 94% theoretical density. At room temperature, the compressibility was  $3.05 \times 10^{12}$  dyn/cm<sup>2</sup>. (The latter corresponds to  $\alpha = 5.3 \times 10^{21}$  cal/cm<sup>2</sup> mole.) These data decrease more rapidly with temperature than the thermodynamic data of Table V-A would indicate.

TABLE I  
Energy Terms in Binary Carbides

<u>Material</u>	<u>E<sub>33</sub></u> <u>kcal/mole</u>	<u>E<sub>3</sub>+E<sub>13</sub>+E<sub>33</sub></u> <u>kcal/mole</u>
ZrC	28.±3.	-35.2± 4.
HfC	15.±8.	-47. ±10.
UC	0	-28.1± 1.6
NbC	15.2±2.5	-28.6± 2.5

TABLE II

A. Metal-Metal Interaction Energy [ $E_{12} - \frac{1}{2}(E_{11}+E_{22})$ ]  
 in Binary Body-Centered Cubic Metal Alloys  
 and on the Metal Sublattice in Ternary Carbides

System	$E_{12} - \frac{1}{2}(E_{11}+E_{22})$ kcal/mole		
	b.c.c. metal	f.c.c. carbide sublattice	difference carbide-metal
Zr-Hf-C	$\geq 0$	$1.86 \pm 0.3$	$1.86 \pm 0.5$
Zr-U-C	$4.4 \pm 0.2$	$6.7 \pm 0.6$	$2.30 \pm 0.8$
Zr-Nb-C	$4.9 \pm 0.3$	$6.5 \pm 0.3$	$1.60 \pm 0.5$
Avg: $1.92 \pm 0.6$			

B. Metal-Metal Distance in Body-Centered Cubic Metals  
 and Face-Centered Cubic Sublattice in Carbides

System	Distance in Å		
	b.c.c. metal	f.c.c. carbide sublattice	difference carbide-metal
Zr	3.11	3.32	.21
Hf	3.07	3.29	.22
Nb	2.86	3.17	.31
U	3.00	3.52	.52
Avg: $.31 \pm .10$			



TABLE III

Dependence on Composition of  $[E_{13}-E_{23}]$  in Ternary CarbideSystem

$$\text{Zr-Nb-C} \quad E_{13}-E_{23} = (1.08 \pm 0.11) - (16.15 \pm 0.44)x \text{ kcal/mole}$$

$$\text{Zr-U-C} \quad E_{13}-E_{23} = (8.5 \pm 0.05) - (23.6 \pm 0.2)x \text{ kcal/mole}$$

$$\text{Zr-Hf-C} \quad E_{13}-E_{23} = (9.6 \pm 0.8) - (7.8 \pm 0.2)x \text{ kcal/mole}$$

TABLE IV

Calculation of  $E_{13}^{\circ}-E_{23}^{\circ}$  in Ternary Carbides

<u>System</u>	<u><math>E_{13}^{\circ}-E_{23}^{\circ}</math> kcal/mole</u>	
	<u>Data from Table III</u> <u><math>E_{13}-E_{23}</math> at <math>x = 0.5</math></u>	<u>Data from Table I</u> <u><math>[E_3-E_{13}+E_{33}]-[E_3+E_{23}+E_{33}]</math></u>
Zr-Nb-C	-7.00±0.5	-6.6± 5
Zr-U-C	-3.3 ±0.2	-7.1± 4.5
Zr-Hf-C	+5.5 ±0.8	11.8±10.8

TABLE V

Evaluation of  $\alpha$ 

## A. From Thermodynamic Data at 2500°K

System	Slope (kcal/mole)	$(r_1 - r_2)^2 \text{ \AA}^2$	$\alpha (10^{21} \text{ cal/cm}^2 \text{ mole})$
Zr-Nb-C	-16.1	0.0144	5.6
Zr-U-C	-23.6	0.0169	4.8
Zr-Hf-C	-7.8	0.0009	43.5

## B. From the Compressibility

$$\alpha = N_0 c r_0 (9/2) (1/\beta)$$

System	$P = (1/\beta) (10^{12} \text{ dyn/cm}^2)$	$r_0 (\text{\AA})$	$\alpha (10^{21} \text{ cal/cm}^2 \text{ mole})$
ZrC	2.2 <sup>(9)</sup>	2.35	7.0
NbC	3.00 <sup>(10)</sup>	2.23	9.0
UC	1.4 <sup>(11)</sup>	2.48	4.7
HfC	2.42 <sup>(10)</sup>	2.32	7.5

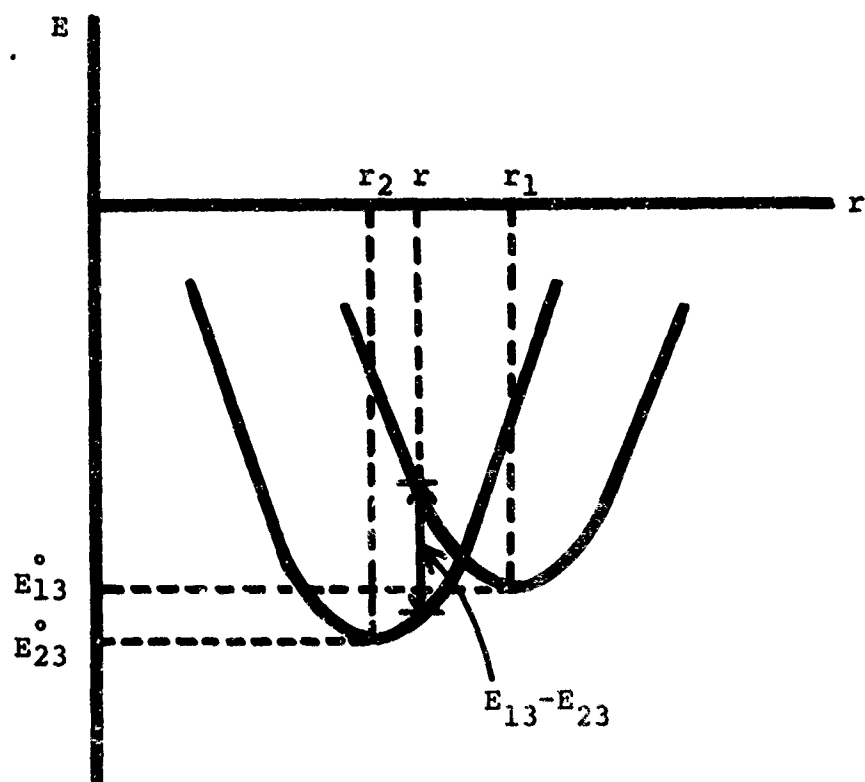


Fig. 1. Schematic Potential-Distance Curves for Two Metal-Carbon Bonds

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DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Wright-Patterson AFB, Ohio		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP
3. REPORT TITLE Thermodynamic Properties of Ternary Refractory Carbides IV. Relations Between Thermodynamic Properties, Bonding, and Compressibility		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report (covers work conducted between 1 July 1967 through 30 June 1969)		
5. AUTHOR(S) (First name, middle initial, last name) M. Hoch and S. Yamauchi		
6. REPORT DATE December 1969	7a. TOTAL NO. OF PAGES 14	7b. NO. OF REFS 13
8a. CONTRACT OR GRANT NO. F33615-67-C-1565 b. PROJECT NO. 7360 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S)  9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFML-TR-69-209 Pt IV	
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Air Force Systems Command Wright-Patterson AFB, Ohio	
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14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	carbides, zirconium, niobium, hafnium, uranium, thermodynamics, activity, compressibility and elastic modulus.						

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